

Investigation of Defects and Polarity in GaN Using Hot Wet Etching, Atomic Force and Transmission Electron Microscopy and Convergent Beam Electron Diffraction

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Availability of reliable and quick methods to investigate defects and polarity in GaN films is of great interest. We have used photo-electrochemical (PEC) and hot wet etching to determine the defect density. We found the density of whiskers formed by the PEC process to be similar to the density of hexagonal pits formed by wet etching and to the dislocation density obtained by transmission electron microscopy (TEM). Hot wet etching was used also to investigate the polarity of MBE-grown GaN films together with convergent beam electron diffraction (CBED) and atomic force microscopy (AFM). We have found that hot H_3PO_4 etches N-polarity GaN films very quickly resulting in the complete removal or a drastic change of surface morphology. On the contrary, the acid attacks only the defect sites in Ga-polar films leaving the defect-free GaN intact and the morphology unchanged. The polarity assignments, confirmed by CBED experiments, were related to the as-grown surface morphology and to the growth conditions.

Introduction Successful fabrication of GaN-based devices depends on the ability to grow epitaxial films on sapphire with low defect density. The poor match in both lattice parameter and thermal expansion coefficient results in a high dislocation density (DD). Wurtzite GaN is a polar material that has two different planes along its *c*-axis. The (0001) plane is the Ga-terminated face while the (000 $\bar{1}$) plane is the N-face [1]. It is known that the surface and bulk properties of GaN layers depend greatly on the polarity [2]. Therefore the availability of reliable and quick methods to determine the defect density and the polarity of GaN films is of great importance.

We have investigated defects in GaN films grown by MBE using PEC method [3] and hot wet etching [4]. We found the whisker density to be similar to the etch pit

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densities (EPD) for samples etched under precise conditions. TEM studies confirmed the DDs obtained by etching which increased our confidence in the validity of the methods used. Additionally, we have demonstrated that hot H_3PO_4 can be used to determine the polarity of GaN films. Already, NaOH and KOH based aqueous solutions at different temperatures have been demonstrated to attack N-polar surface whereas the morphology of Ga-polar GaN films remains unchanged [5–7]. Similarly, we found that a few seconds of etching in hot H_3PO_4 leads to the complete removal or a drastic change in the morphology of N-polar GaN films. On the contrary, a defect free Ga-polar film is hardly affected by the hot acid. Only hexagonal pits associated with the surface defects are formed after several minutes of etching. The polarity assignments, confirmed by CBED experiments, were related to the as-grown morphology and to the growth conditions. We found that the GaN films grown by MBE on high temperature (HT) AlN ($> 890^\circ\text{C}$) and GaN ($770\text{--}900^\circ\text{C}$) buffer layers show Ga- and N-polarity, respectively [8].

Experimental Details The GaN samples consisted of unintentionally n-doped GaN layers grown by MBE on *c*-plane of sapphire using radio-frequency activated N. Some samples utilized GaN buffer layers grown at 800°C (HT). Others utilized AlN buffer layers grown at $890\text{--}930^\circ\text{C}$ (HT). Following the buffer layers, $\approx 1\ \mu\text{m}$ thick GaN layers were grown at a temperature between 720 and 850°C with growth rates in the range of $0.3\text{--}1\ \mu\text{m/h}$ under N-limited (Ga-rich) conditions. PEC etching was carried out in a standard electrochemical cell at room temperature using a 0.02M KOH solution and a He–Cd laser. Further details of the PEC experimental set-up can be found elsewhere [9, 10]. The morphology of samples etched by PEC and wet etching was investigated using AFM and scanning electron microscopy (SEM). Additionally, some samples were observed by TEM to estimate the DD. The polarity was determined by hot H_3PO_4 etching, CBED experiments and AFM investigation of their as-grown morphology. Additionally, in-situ RHEED patterns during the MBE growth supported the polarity assignments.

Results and Discussion PEC etching has been demonstrated to be suitable for DD estimation in n-type GaN films. Freestanding whiskers were obtained by selectively etching GaN between dislocation sites under precise etching conditions. With XTEM analysis, the presence of the dislocations in the whiskers was demonstrated and the whisker density was found close to the DD [3]. We used slightly carrier-limited conditions to etch Ga-polar GaN selectively, leaving threading vertical wires on the surface.

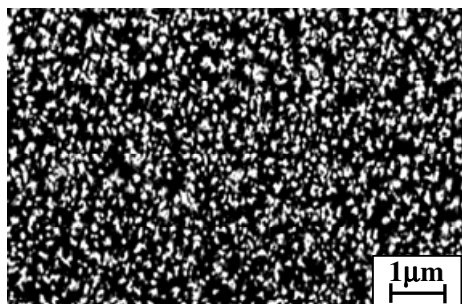


Fig. 1. Plan-view SEM image of the PEC etched sample. The density of the whisker-like features (white dots in the image) is $\approx 1\text{--}2 \times 10^9\ \text{cm}^{-2}$

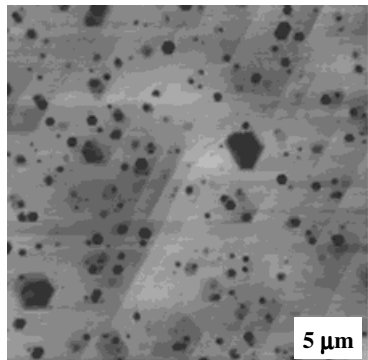


Fig. 2

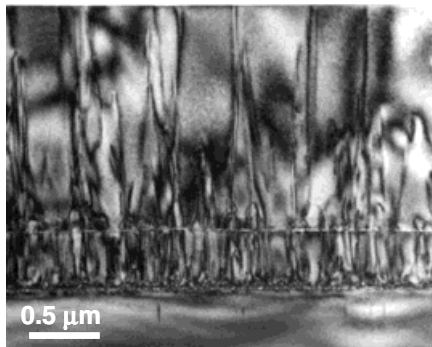


Fig. 3

Fig. 2. AFM image of the Ga-polar GaN surface morphology after etching in H_3PO_4 for 5 min at 160°C . The EPD is $\approx 1 \times 10^9 \text{ cm}^{-2}$. The vertical scale ranges from 0 to 10 nm

Fig. 3. Cross-sectional TEM image of a Ga-polar GaN layer. The total DD, near the top surface, is about $4 \times 10^9 \text{ cm}^{-2}$ (edge dislocations about 95% of the total)

The density of features (white dots in the SEM image of Fig. 1) formed by the PEC process is $\approx 2 \times 10^9 \text{ cm}^{-2}$, the same value obtained from the AFM investigation.

Wet etching is a suitable technique to determine in Ga-polar GaN the density of defects propagating to the surface. We have used hot H_3PO_4 as a defect etchant, which produces hexagonal pits at the defect sites. During etching, a careful balance must be struck to ensure that every defect is delineated, but not over-etched to cause merging which would lead to an underestimation of the defect density. H_3PO_4 for 5 min at 160°C was used to determine the defect density in Ga-polar GaN films grown by MBE. The AFM image of Fig. 2 shows the etched surface with EPD of $\approx 1 \times 10^9 \text{ cm}^{-2}$. TEM analyses were carried out in order to determine the effective DD. From XTEM observation (Fig. 3), the threading dislocations were observed starting from the buffer/GaN interface and propagating within the GaN layer. The total DD, near the surface, including screw ($< 1 \times 10^7 \text{ cm}^{-2}$), mixed ($\approx 1 \times 10^8 \text{ cm}^{-2}$) and edge dislocations (about 95% of the total) is $\approx 4 \times 10^9 \text{ cm}^{-2}$ close to the values obtained by defect revealing etches.

It is known that the electrical and optical properties of GaN layers depend greatly on the polarity. We have investigated the polarity of GaN films grown by MBE on HT ($T > 770^\circ\text{C}$) GaN buffer layers or HT ($T \approx 900^\circ\text{C}$) AlN buffer layers in order to obtain N- and Ga-polar GaN films, respectively. The polarity was determined by etching in hot H_3PO_4 and AFM imaging of as-grown surface morphologies. The polarity assignments were supported by in-situ RHEED patterns and confirmed by CBED experiments. As reported in the literature, the surface of a Ga-polar film is either very flat or shows stepped terraces. The surface of a N-polar film grown by MBE shows tall columns or terraces separated by deep troughs. Similar to NaOH- and KOH-based etchings, we have found that hot H_3PO_4 etches N-polar GaN films very quickly resulting in the complete removal or a drastic change of the morphology as revealed by AFM or optical microscopy. The etching rate is from 0.3 to $0.7 \mu\text{m}/\text{min}$. On the contrary, a defect free Ga-polar film is hardly affected by the hot acid. As shown in Fig. 2, only hexagonal pits associated with the surface defects are formed after several minutes of etching of Ga-polar films.

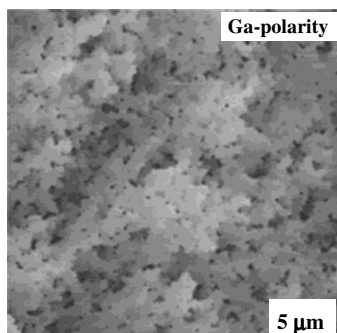


Fig. 4

Fig. 4. AFM image of Ga-polar GaN sample. The rms roughness is ≈ 1.3 nm. The vertical scale ranges from 0 to 20 nm

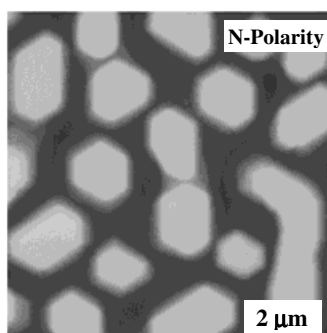


Fig. 5

Fig. 5. AFM image of N-polar GaN sample. The rms roughness is ≈ 20 nm. The vertical scale ranges from 0 to 80 nm

The surface morphology of an as-grown Ga-polar GaN film is shown in Fig. 4. A HT AlN buffer layer leads to Ga-polar film with a smooth, but pitted surface morphology with a rms roughness of ≈ 1.3 nm. According to the literature, the Ga-polar film shows a 2×2 RHEED pattern upon cool-down at temperatures between 280 and 650 °C. Shown in Fig. 5 is the typical surface morphology of a N-polar film obtained using a HT GaN buffer layer. The rough morphology presents 50–100 nm high non-coalesced columns with a rms roughness as high as 20 nm. The RHEED pattern upon cooling shows only the bulk 1×1 structure. Dipping of the N-polar GaN layer in hot (160 °C) H_3PO_4 for only 20 s results in a drastic change of the morphology. Longer dipping in hot H_3PO_4 for just few minutes instead results in the complete removal of the film, obtaining the clean surface of sapphire substrate by AFM imaging. In the AFM image of Fig. 6, we show the surface morphology of a N-polar film after etching in hot H_3PO_4 for 20 s. Etching of the *c*-plane with an etch rate of ≈ 0.5 $\mu\text{m}/\text{min}$ produces 300–400 nm high features on the sapphire substrate (rms roughness ≈ 150 nm).

In order to confirm the polarity assignments, we carried out CBED experiments. For a GaN layer grown on HT AlN buffer layer, the CBED study confirmed the Ga-polarity, whereas from XTEM study the density of inversion domains (ID) was estimated $\approx 1 \times 10^7 \text{ cm}^{-2}$.

For a GaN layer grown on HT GaN buffer layer, the CBED study again confirmed the assigned N-polarity, whereas from TEM study the density of IDs was estimated $\approx 1 \times 10^{11} \text{ cm}^{-2}$.

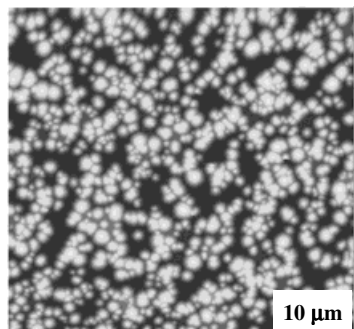


Fig. 6. AFM image of N-polar GaN morphology after etching in H_3PO_4 for 20 s at 160 °C. The rms roughness is ≈ 150 nm. The vertical scale ranges from 0 to 1200 nm

Conclusion PEC and hot wet etching experiments were carried out to determine the defect density in GaN films. The density of whiskers formed by the PEC process was similar to the density of pits formed by wet etching and close to the DD obtained by TEM. Hot wet etching has been used also to determine the polarity of MBE-grown GaN layers. We found that few seconds of etching in H_3PO_4 produce a drastic change of the morphology whereas few minutes result in the complete removal of N-polar GaN film. On the contrary, the hot acid attacks only the defect sites in Ga-polar films producing pits, but leaving the defect-free GaN intact and the morphology unchanged after several minutes of etching.

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